Things of science

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SILICONES

Unit No. 263

SILICONES

This unit of THINGS of science consists of a piece of silicon, silicone-treated cloth, silicone-treated paper, silicone rubber, silicone oil and antifoam.

Silicon, from which the various silicone products like those in this unit are made, is a nonmetalic element widely distributed in nature and is exceeded only by oxygen in abundance.

Silicon is not found free in nature, but is combined with oxygen in the form of a variety of silicates. In this form it is found in rocks and sand and composes about 87% of the earth's crust. Hundreds of mineral silicates occur in nature. You are all familiar with natural silicates, such as quartz, feldspar, mica and asbestos. Although many of us are not familiar with silicon as such, it has a very important place in our lives. For centuries, silicates have been used to make glass and other ceramics.

This unit deals with silicon in another form, as new compounds, silicones, manmade through chemistry.

The specimens and experiments in this unit will acquaint you with some forms of the silicones, their behavior and uses.

Experiment 1. First identify your specimens.

SILICON—Small chip of gray, metallic-looking material.

SILICONE RUBBER — One extruded length.

SILICONE GREASE—Greaselike material in plastic envelope.

SILICONE OIL—Vial of clear oil.

ANTIFOAM—Vial of milky liquid.

TREATED CLOTH—A specimen of silicone-treated cloth.

TREATED PAPER—A specimen of silicone-treated paper.

Experiment 2. Take the sample of silicon (Si) from the box and observe its gray, metallic appearance. Note how shiny and hard it is. Although it looks like metal, it belongs to the nonmetal group in chemical classification. In the periodic table of elements, it is found in group IV, in the same group as carbon.

It is hard and brittle and has the same crystal structure as diamond. Like diamonds, it will scratch glass. Take your piece of silicon and try scratching a piece of glass.

Since silicon never occurs naturally the piece of silicon you have in your unit was prepared by chemical process from quartz

(silicon dioxide). Silicon is usually produced industrially by reducing silicon dioxide, with carbon, at high temperatures in an electric furnace. The reaction that takes place is

$$\underset{\text{silicon dioxide}}{SiO_2} + \underset{\text{carbon}}{2\,C} = \underset{\text{silicon}}{Si} + \underset{\text{carbon monoxide}}{2\,CO}$$

Silicon is not an active element at ordinary temperatures and does not oxidize readily. At high temperatures, however, it will combine with oxygen to form silicon dioxide.

CHEMISTRY

Silicones may best be described as a new class of synthetic man-made chemicals combining the best qualities of sand, coal and oil in a way not found in nature.

The name silicones was first applied to these compounds by F. S. Kipping and his students in England about 1900. These new organosilicon compounds were believed to be similar in structure to the organic compounds known as ketones. They were therefore called "silicoketones" or "silicones." Although they were later found to be unrelated to ketones, the name silicone was retained.

Strictly speaking, the name silicones should be applied only to silicon polymers containing silicon-oxygen-silicon linkages and containing a significant proportion of organic groups directly attached to silicon.

In structure, silicones are similar to silicate minerals in that both have the linkage of silicon and oxygen, —Si—O—Si—. However, in the silicones, carbon atoms are also linked to the Si atom in addition to the oxygen, thus a simplified silicone containing methyl (CH_3—) groups has the structure,

$$
\begin{array}{ccccccccc}
 & CH_3 & & CH_3 & & CH_3 & & CH_3 & \\
 & | & & | & & | & & | & \\
—O— & Si & —O— & Si & —O— & Si & —O— & Si & —O— \\
 & | & & | & & | & & | & \\
 & CH_3 & & CH_3 & & CH_3 & & CH_3 &
\end{array}
$$

silicone

Silicon, derived from quartz, is the inorganic element in the compound and gives the silicone its quality of resistance to heat, cold, chemicals and weather, that is, its stability. The organic group, CH_3—, the hydrocarbon part, gives silicones their flexibility. It is this flexibility which makes silicones useful in a wide range of applications that require both stability and flexibility. By varying the proportions the synthesis from silica to silicone and

and types of the organic members, as well as the size of the molecules, the chemist has been able to produce silicones that range in physical form all the way from volatile liquids to stable solids.

Because silicones are derived from silica (quartz) it is commonly thought that these compounds are composed of fine particles of sand or quartz. However, on the contrary, the silicones have undergone a complete chemical transformation in are actually smooth in texture completely devoid of any grainy quality, as you will observe in the silicone oil (Experiment 4), and resemble organic rubber and oils. Many silicone oils, in fact, are used in furniture polishes because they are suitable for polishing the most delicate surfaces.

If the silicone chain has less than 20 of the grouping

$$\begin{array}{c} CH_3 \\ | \\ —Si—O— \\ | \\ CH_3 \end{array}$$

in its molecular chain, the silicone is an oil, like the sample in your unit. A silicone containing several thousands of this grouping in the chain will be a solid, such as the sample of silicone rubber.

A part of the chain structure of natural rubber is

$$
\begin{array}{ccccccccccccccccc}
 & H & & & & H & & H & & H & & & & H & & H & \\
 & | & & & & | & & | & & | & & & & | & & | & \\
- & C & - & C & = & C & - & C & - & C & - & C & = & C & - & C & - \\
 & | & & | & & & & | & & | & & | & & & & | & \\
 & H & & CH_3 & & & & H & & H & & CH_3 & & & & H &
\end{array}
$$

The essential difference between the silicone polymers and organic polymers can be observed from the two structural formulas. The organic polymers are made up of a backbone of carbon-to-carbon atoms linked together.

The silicone rubbers differ from natural rubber in that their backbone structure is made up of silicon-oxygen linkages. This silicon-oxygen linkage, as mentioned above, is the same bond that is found in other high-temperature materials, such as quartz, glass and sand. This is the reason for the outstanding high-temperature properties of silicones and their general inertness toward many deteriorating effects.

The four basic properties of silicones are:

1. Resistance to temperature extremes (—100°F to 600°F).

2. Release from sticking.

3. Unusual surface properties (i.e., suppress foam, repel water, etc.).

4. Inertness.

The main forms of silicones made today are rubbers, fluids, resins, emulsions, specialties and intermediates.

Experiment 3. Look at your samples of silicone products, the oil, antifoam liquid, grease and extruded rubber. Here you have some typical kinds of silicones.

Silicones are used as heat-transfer fluids, sealants, defoamers, protective and non-stick coatings, electrical insulation, polish and paint additives and for a variety of other purposes.

The transition from the academic to the industrial approach to silicones took place in the early 1930's. In the United States, early in that decade, interest began to grow in the laboratories of General Electric Company and the Corning Glass Works in insulating materials which would withstand a temperature far above 105°C. At General Electric, Dr. Winton Patnode initiated work in the field of organosilicon compounds by his investigations of silicate ester polymers. At Corning Glass, Dr. J. Franklin Hyde was experimenting with organosilicon compounds and their polymers.

One of the most significant breakthroughs of that period was the devel-

opment of the "direct process" by Dr. Eugene Rochow at General Electric's Research Laboratory in Schenectady, who discovered that alkyl and arylsilicon halides could be produced by the direct reaction of the alkyl and aryl halides with powdered metallic silicon. This was the first economical process for manufacturing silicones on a commercial scale and is the key to today's manufacture of basic silicones throughout the world. By 1944 silicone rubber appeared, with the announcement by General Electric that it had developed the material.

The silicone industry has grown over the years, until today, the U. S. market for the materials is upward of $60 million.

PHYSICAL NATURE

Obtain a small amount of yellow petroleum motor oil (SAE 30, Pennsylvania paraffinic stock oil available at any gas station).

Experiment 4. Smell the silicone oil included in this unit. You will find that it has no odor. It is also tasteless. The specimen of silicone oil is an example of a silicone in its purest form.

Smell the motor oil. It has the distinctive odor of petroleum oil with which you are all familiar.

Take a drop of the silicone oil between your fingers and feel its consistency. Notice its smooth, oily feeling.

Silicone fluids may be classified into two composition groups, the dimethyl silicones and silicones other than dimethyl. The first group has two methyl (CH_3) groups for each silicon atom. In the second group some of the methyl radicals are replaced by some other organic radical, sometimes ethyl but usually phenyl. The phenyl types are stable at higher temperatures and have slightly better lubricity than dimethyl silicone fluids.

The oil in this unit is a dimethyl type of silicone oil.

Experiment 5. Silicones have defoaming properties. Partly fill a small jar with water and add a small quantity of household detergent or powdered soap to the water. Put the cover on the jar and shake until rich suds are obtained. Remove the cover and add a drop or two of the defoaming agent (milky fluid). Stir the mixture with a spoon. What happens?

What produces this effect? Foam is caused by the entrapment of air or vapors beneath the surface of a liquid, such as soaps, detergents or other foam-producing substances. Silicones have a comparatively

low surface tension. When added to a foaming liquid, the absence of high surface tension causes them to spread out quickly to envelop the surface of the bubbles of foam which are like large elastic balloons. The chemical dissimilarity of the silicones to the foamy film causes weak spots with the resulting collapse of the foam. This action is analogous to that of a pin piercing a balloon.

Silicone antifoam agents are often used in automotive crankcase oil to reduce foaming caused by other common additives. They are also used in the processing of petroleum oils, latex coatings and adhesives.

Experiment 6. To demonstrate the low surface tension of the defoaming liquid, cut two strips of letter paper about two inches long and a quarter of an inch wide. Place these close together in a shallow dish of water. Place a drop of the defoaming liquid between the two pieces. See how quickly and suddenly they spread apart. The defoaming liquid reduces the surface tension between the strips of paper which are then pushed apart by the greater surface tension in the outer unaffected area.

The quick action of the defoamer is

indicated by the suddenness with which the papers separate.

Experiment 7. Take the silicone-treated cloth. Feel its texture. Place a few drops of water on the cloth. What happens? The water beads up into droplets and does not readily penetrate the cloth. The silicone with which the material was treated has made it water-repellent.

Experiment 8. Crush the cloth in your hand. Note that it wrinkles with difficulty. Spread water on the surface and then dry. The wrinkles disappear. The silicone treatment has made the cloth wrinkle-resistant.

Experiment 9. Pour a few drops of hot coffee or tea on the cloth. Shake the cloth and remove any excess moisture on the surface. The liquid leaves no stain on the cloth. This experiment illustrates two other important properties of silicones when used as water-repellent coatings. They will protect from waterborne stains, even where heat that would destroy wax-containing, water-repellent materials is present.

Experiment 10. Hold the treated cloth up to the light. Is the light visible through it? The silicone treatment does not fill

the pores of the material. Thus permitting the fabric to "breathe" and provide normal air circulation essential to the comfort of the wearer.

Silicones are also used to make masonry water-repellent. In the same way, the silicone lines the pores of the masonry instead of forming a barrier film. It repels penetration of moisture, but does not interfere with the circulation of air and permits evaporation of moisture from within.

Experiment 11. Take your silicone-treated paper. Note its texture and strength.

Take a piece of cellophane tape and apply it to an ordinary piece of paper. Now try to remove it. What happens?

Try to apply a piece of cellophane tape to the silicone-treated paper. What is the result? Note how the tape refuses to stick at all.

This demonstrates another property of silicones—they resist sticking. For this reason many sticky substances are packaged in cartons treated with silicones. Even hot asphalt poured into a paper container treated with silicones will not stick.

Experiment 12. Take a pen and try

writing on the treated paper. What is the result? The treated paper is also stain-resistant.

Experiment 13. Take a piece of ordinary untreated paper and the treated paper. Submerge them both in a glass of water for one or two minutes. Remove the untreated paper and pull it apart. You will find that it tears readily.

Try to do the same with the silicone-treated paper. Is it stronger? This is called wet strength. Shipping cartons and bags for cement and other materials are often treated with silicones so that they will resist breaking even when wet.

This is another example of the water-repellent properties of silicones.

Experiment 14. Wipe dry the piece of silicone-treated paper. Rub it between your fingers. Does it have a waxy feeling? Try to scrape the silicone surface off with your fingernails. You will find that your fingernail cannot penetrate the surface.

HIGH-TEMPERATURE RESISTANCE

Experiment 15. Take the treated paper and, holding it with a pair of tongs or other metal holder, place it over a flame. *Do not let the paper catch fire.*

in its center. Place in a pan and heat. What happens to the rubber?

Experiment 20. Take your piece of silicone rubber. Repeat the experiment. Does the silicone rubber melt? Silicone rubber also resists heat and remains unaffected by temperatures that will melt natural rubber. Cool and stretch the silicone rubber. It retains its elasticity and is just as flexible as before.

LOW-TEMPERATURE PROPERTIES

For the following experiment obtain some dry ice. Handle dry ice with care. DO NOT TOUCH WITH YOUR FINGERS—USE TONGS OR HEAVY GLOVES. DO NOT PUT IN A CLOSED CONTAINER.

Experiment 21. Place some pieces of dry ice in a metal container the size of a cup. With tongs or other holder, place the silicone rubber and a small length of natural rubber, a rubber elastic band, in the dry ice bath. Leave for a few minutes. DO NOT COVER THE CONTAINER. Using the tongs, remove the specimens.

Compare the two pieces. Note how stiff and hard the natural rubber has become.

Observe how flexible and elastic the silicone rubber has remained.

Experiment 22. Take some of the silicone grease and spread it on a piece of aluminum foil. Do the same with some household grease or vaseline. Lower both carefully into the dry ice with the tongs. After ten minutes remove from the dry ice and observe the condition of the two samples. Which of the two has become hard and stiff? The silicone grease remains soft.

The experiment demonstrates the ability of silicone grease to lubricate at temperatures which stiffen conventional grease. Continued exposure of the silicone grease may also result in freezing the silicone grease. However, the experiment shows that the low temperature capabilities of silicone lubricating grease are much better than those of conventional types.

Experiment 23. Repeat the same procedure with silicone oil and petroleum oil. What are your results?

Silicone oils and fluids can function at lower temperatures than conventional oils. The silicones remain free-flowing even at low temperatures. This is significant, since

the operation of many types of equipment relies on the ability of lubricants to remain in a form that can be pumped, even at the lowest temperatures.

The low-temperature flexibility of silicones is difficult to explain. It is not a property inherent in the silicon-oxygen bond. It can be said, however, that the more irregularly shaped atoms and molecules in silicone polymers do not line up and crystallize (freeze) as easily as most organic materials.

The experiments in this unit have illustrated what are considered the most important properties of silicones: resistance to temperature extremes; release from sticking and their unusual surface properties (suppressing foam, repelling water); and general inertness to environment.

References to silicones can be found in standard chemistry books.

Excellent references in this field are:

Meals, Robert M. and Frederick N. Lewis, *Silicones,* Reinhold Publishing Corp., 1959.

Rochow, Eugene G., *An Introduction*

to the Chemistry of Silicones, John Wiley & Sons, 1961.

This unit was prepared with the co-operation of the General Electric Company, Silicone Products Department, Waterford, N. Y., who supplied the samples of silicon and silicones.

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Production by Ruby Yoshioka

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